

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
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in its capacity as elected Office

Date of mailing (day/month/year)

15 March 2000 (15.03.00)

International application No.

PCT/GB99/02480

Applicant's or agent's file reference

M035DTD4063

International filing date (day/month/year)

28 July 1999 (28.07.99)

Priority date (day/month/year)

29 July 1998 (29.07.98)

Applicant

MERTENS, Machteld, M. et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

16 February 2000 (16.02.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
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Authorized officer

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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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by fax and post

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CASE NO. 4063 (1)			
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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 01.12.2000

Applicant's or agent's file reference
M035DTD4063(1)

IMPORTANT NOTIFICATION

International application No.
PCT/GB99/02480

International filing date (day/month/year)
28/07/1999

Priority date (day/month/year)
29/07/1998

Applicant
EXXON CHEMICAL PATENTS, INC. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference M035DTD4063(1)	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/02480	International filing date (<i>day/month/year</i>) 28/07/1999	Priority date (<i>day/month/year</i>) 29/07/1998
International Patent Classification (IPC) or national classification and IPC C01B37/04		
Applicant EXXON CHEMICAL PATENTS, INC. et al.		



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 16/02/2000	Date of completion of this report 01.12.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Schmidt, O Telephone No. +49 89 2399 8438 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02480

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-25 as originally filed

Claims, No.:

1-24 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/02480

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	3-7, 17-18, 20
	No:	Claims	1-2, 8-16, 19, 21-24
Inventive step (IS)	Yes:	Claims	3-7, 17-18, 20
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-24
	No:	Claims	

- 2. Citations and explanations**
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

SECTION V.:

1. Reference is made to the following documents:

D1: Alan Dyer, "An introduction to molecular sieves", John Wiley & Sons (1988), pages 136-139

D2: EP-a-0 753 485 (EXXON CHEMICAL PATENTS INC) 15 January 1997 (1997-01-15)

Do: EP-a-0 110 650 (MOBIL OIL CORP) 13 June 1984 (1984-06-13)

Document D1 was not cited in the International Search Report and a copy of the document has already been forwarded to the Applicant.

2.

- 2.1 Document D1 discloses that crystalline molecular sieves or zeolite of the type aluminophosphate or ALPO_4 and silica-aluminophosphate or SAPO, for example SAPO-34, and of various structure types like Chabazite, Leyvnite or Faujasite and the aluminium in said zeolite may be partially substituted by other metals. D1 further discloses the use of such zeolite in hydrocarbon conversion, adsorption, separation and the like (cf. D1; pages 136-139). Therefore, the subject-matter of claims 19 and 21-23 is no longer novel with respect to D1. Document D1 does not disclose, however, seeding a synthesis mixture for ALPO's or SAPO's with colloidal crystalline molecular sieve seeds.

Therefore, the subject-matter of claims 19 and 21-23 does not meet the requirements of Article 33(2) PCT for lack of novelty with respect to D1.

- 2.2 Document D2 discloses a process for the manufacture of a zeolite containing aluminium and silicon which may be partly or wholly replaced by phosphorus in its framework - although the examples in D2 only disclose aluminosilicate molecular sieves - which process comprises hydrothermally treating a synthesis mixture comprising the respective elements necessary to form said zeolite and colloidal zeolite seeds, the latter are used to control the quality and the particle size of the

product and/or accelerate the formation of the product. The seeds in D2 may be in the form of a suspension and of the Offretite structure type with a particle size within the range of 25-90 nm and in very small proportion of less than or equal to 0.1 wt% based on the total weight of the synthesis mixture. The zeolite in D2 may be either in particulate form or in the form of a layer on a support such as in the form of a membrane and if desired after washing, ion exchange and/or calcination said zeolite are used as catalysts in hydrocarbon conversion, adsorption or separation processes (cf. D2; claims 1, 5-7, 11, 13-15; page 2, lines 7-33 and page 3, lines 12-48).

Therefore, the subject-matter of claims 1-2, 8-16, 19, 21 and 23-24 does not meet the requirements of Article 33(2) PCT for lack of novelty with respect to D2.

- 2.3 Document D3 discloses a process for the manufacture of a zeolite containing aluminium and silicon which may be partly or wholly replaced by phosphorus and/or nickel in its framework - although the examples in D3 only disclose aluminosilicate molecular sieves - which process comprises hydrothermally treating a synthesis mixture comprising the respective elements necessary to form said zeolite and colloidal zeolite seeds, the latter are used to control the quality and the particle size of the product and/or accelerate the formation of the product. The seeds in D3 have a particle size of less than 100 nm and are in particulate form and if desired after washing, ion exchange and/or calcination said zeolite are used as catalysts in hydrocarbon conversion, adsorption or separation processes (cf. D3; claims 1, 9, 11, 13-14; examples 1 and 5; page 2, lines 10-26; page 3, lines 5-16; page 4, lines 22-28; page 5, lines 1-16 and page 8, lines 14-17).

Therefore, the subject-matter of claims 1-2, 14-16, 19, 21 and 23-24 does not meet the requirements of Article 33(2) PCT for lack of novelty with respect to D3.

- 2.4 None of the subject-matter of claims 3-7, 17-18 and 20 is disclosed in any of the aforementioned documents of the prior art.

The subject-matter of claims 3-7, 17-18 and 20 meets the requirements of Article 33(2)(3) PCT.

2.5 The subject-matter of claims 1-24 meets the requirements of Article 33(4) PCT.

SECTION VIII.:

3. The subject-matter of claim 1 is unclear to the extent that it is not disclosed which elements are necessary to form the phosphorus-containing molecular sieve and which colloidal crystalline molecular sieve seeds are used. Moreover the statement "... for a time and at a temperature appropriate to form the desired molecular sieve." in claim 1 defines the process in terms of a general result to be achieved and thus leads to a lack of clarity of the claim as a whole as the choice of these important process parameters is left open.

The subject-matter of claim 2 is unclear to the extent that it is not apparent which are the other optional elements.

Therefore the subject-matter of claims 1 and 2 does not meet the requirements of Article 6 PCT for lack of clarity.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB99/02480 (22) International Filing Date: 28 July 1999 (28.07.99) (30) Priority Data: 9816505.3 29 July 1998 (29.07.98) GB 9816508.7 29 July 1998 (29.07.98) GB (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS, INC. [US/US]; 5200 Bayway Drive, P.O. Box 2149, Baytown, TX 77522 (US). (71) Applicant (for GB only): EXXON CHEMICAL LIMITED [GB/GB]; 4600 Parkway, P.O. Box 122, Fareham, Hants PO15 7AP (GB). (71) Applicant (for US only): VAN DEN BERGE, Jannetje, M. (legal representative of the deceased inventor) [NL/NL]; Fazantenlaan 26, NL-3233 BB Oostvoorne (NL). (72) Inventor: VERDUIN, Johannes, P. (deceased). (72) Inventors; and (75) Inventors/Applicants (for US only): MERTENS, Machteld, M. [BE/BE]; Beringstraat 72, B-3190 Boortmeerbeek (BE). MORTIER, Wilfried, J. [BE/BE]; Diestse Steenweg		(483) B-3010 Kessel-Lo (BE). JANSSEN, Marcel, J., G. [NL/BE]; Domeinstraat 84, B-3010 Kessel-Lo (BE). VAN OORSCHOT, Cornelius, W., M. [NL/BE]; Ploegsebaan 136, B-2930 Brasschaat (BE). VAUGHAN, David, E., W. [US/US]; 1109 Croton Road, Flemington, NJ 08822 (US). (74) Agents: DARBY, David, Thomas et al.; Abel & Imray, 20 Red Lion Street, London WC1R 4PQ (GB). (81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.	
(54) Title: PROCESSES FOR MANUFACTURE OF MOLECULAR SIEVES			
(57) Abstract Colloidal crystalline molecular sieve seeds are used in phosphorus-containing crystalline molecular sieve manufacture. Certain of the products have enhanced utility in oxygenate conversions.			

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PROCESSES FOR MANUFACTURE OF MOLECULAR SIEVES

This invention relates to molecular sieves and processes
5 for their manufacture. More especially it relates to
processes in which synthesis mixtures are seeded to control
process conditions and product characteristics. The
invention relates primarily to the manufacture of phosphorus-
containing molecular sieves.

10 It is well-known that seeding a molecular sieve
synthesis mixture frequently has beneficial effects, for
example in controlling the particle size of the product,
avoiding the need for an organic template, accelerating
synthesis, and improving the proportion of product that is of
15 the intended structure type.

In U.S. Patent No. 4 440 871, the preparation of a
number of phosphorus-containing molecular sieves is
described, and it is stated that the crystallization
procedure may be facilitated by stirring, or other moderate
20 agitation of the synthesis mixture, or by seeding it with
crystals of the molecular sieve to be produced or one of a
topologically similar structure.

The patent particularly describes processes for the
manufacture of numerous crystalline microporous
25 silicoaluminophosphates (SAPO's) including SAPO-34, employing
sources of silicon (e.g., a silica sol), aluminium (e.g.,
hydrated aluminium oxide), and phosphorus (e.g.,
orthophosphoric acid), and an organic template, for example
tetraethylammonium hydroxide (TEAOH), isopropylamine (iPrNH₂)
30 or di-n-propylamine (DPA). The patent, the disclosure of
which is incorporated by reference herein, gives X-ray
diffraction data for the SAPO's and describes their utilities
in catalysis and absorption.

It has now been found that advantages result from the use of colloidal seeds in the manufacture of phosphorus-containing molecular sieves.

The present invention accordingly provides in a first aspect a process for the manufacture of a crystalline molecular sieve containing phosphorus in its framework, which process comprises treating a synthesis mixture comprising elements necessary to form the phosphorus-containing molecular sieve and colloidal crystalline molecular sieve seeds for a time and at a temperature appropriate to form the desired molecular sieve.

It has surprisingly also been found that the seed crystals may be of a structure type different from that of the desired molecular sieve. Such seeding may be regarded as "heterostructural", whereas seeding with seeds of the same structure type is termed "isostructural", whether or not the seeds are of the same composition (i.e., contain the same elements in the same proportions) as the crystalline molecular sieve to be produced.

Where the seeds are of a structure type different from those of the desired molecular sieve, advantageously the seeds and the desired molecular sieves are topologically similar, for example are members of the ABC-6 group of materials, as described in "Topochemistry of Zeolites and Related Materials", J.V. Smith, Chem. Rev. 1988, 88, 149 at 167, the disclosure of which review article is incorporated herein by reference. The ABC-6 group includes, *inter alia*, the Offretite, Chabazite and Levyne structures.

As used in this specification, the term "structure type" is used in the sense described in the Structure Type Atlas, Zeolites 17, 1996.

The present invention accordingly provides in a second aspect a process for the manufacture of a crystalline molecular sieve containing phosphorus in its framework, which

comprises treating a synthesis mixture comprising elements necessary to form a phosphorus-containing molecular sieve of a first structure type and colloidal molecular sieve seed crystals of a second, different, structure type, for a time
5 sufficient and at a temperature appropriate to form the molecular sieve of the first structure type.

In further aspects, the invention provides the use, in the synthesis of a phosphorus-containing crystalline molecular sieve, of colloidal seed crystals to control the
10 particle size of the product, or to accelerate the formation of the product, or both to control the particle size and accelerate the formation of the product.

As the phosphorus-containing molecular sieves to be prepared by the processes of the invention, there may be
15 mentioned more especially aluminophosphates and silicoaluminophosphates. As examples of structure types produced there may be mentioned more especially molecular sieves of the structure types CHA and LEV. As seeds, there may for example be used crystals of structure type LEV, OFF,
20 and CHA. As specific materials to be used, there may be mentioned Levyne, ZSM-45, Chabasite, Offretite and SAPO-34.

The seeds used in the present invention may be obtained by methods described herein or known in the art or described in the literature.

25 Manufacture of OFF-structure type seed crystals, in particular colloidal Offretite seeds, may be carried out as described in International Application No. WO 97/03020, while suitable procedures, including details of synthesis mixtures and hydrothermal treatment, for the manufacture of LEV- and
30 CHA- structure type crystals are described in EP-A-91048, 91049, 107 370, 143 642 and U.S. Patent No. 4 495 303 (for LEV) and GB-A-868 846 and 2 061 500 and U.S. Patents Nos. 3 030 181 and 4 544 538 (for CHA), the disclosures of all of which are incorporated by reference herein. Manufacture of

CHA- and LEV-structure type seed crystals is advantageously carried out as described in the examples below.

Apart from the presence of the seeds, the synthesis mixture used in the present invention is typically one that
5 is known in the art or as described in the literature as suitable for the production of the molecular sieve concerned. This is also the case for the conditions of treatment, except that the presence of the seeds may make possible the reduction of reaction times or may obviate stirring if that
10 were otherwise necessary.

In general, the treatment of the synthesis mixture to yield the desired phosphorus-containing crystalline molecular sieve, usually termed hydrothermal treatment, though strictly that term should be used only for treatments in which there
15 is vapour-phase water present, is advantageously carried out under autogenous pressure, for example in an autoclave, for example a stainless steel autoclave which may, if desired, be ptfе-lined. The treatment may, for example, be carried out at a temperature within the range of from 50, advantageously
20 from 90, especially 120, to 250°C, depending on the molecular sieve being made. The treatment may, for example, be carried out for a period within the range of from 20 to 200 hours, preferably up to 100 hours, again depending on the molecular sieve being formed. The procedure may include an ageing
25 period, either at room temperature or, preferably, at a moderately elevated temperature, before the hydrothermal treatment at more elevated temperature. The latter may include a period of gradual or stepwise variation in temperature.

30 For certain applications, the treatment is carried out with stirring or with rotating the vessel about a horizontal axis (tumbling). For other applications, static hydrothermal treatment is preferred. If desired, the synthesis mixture may be stirred or tumbled during an initial

part of the heating stage, for example, from room temperature to an elevated, e.g., the final treatment, temperature, and be static for the remainder. Agitation generally produces a product with a smaller particle size and a narrower particle size distribution than static hydrothermal treatment.

The seeds are generally present in the synthesis mixture in a concentration of up to 10000, advantageously at most 3000, more advantageously at most 1500, and preferably at most 1000, more preferably at most 500, and most preferably at most 350 ppm, based on the total weight of the synthesis mixture. A minimum seeding level is generally 1 ppb (0.001 ppm), advantageously at least 0.1, more advantageously at least 1, and preferably at least 10, ppm, based on the total weight of the synthesis mixture. Advantageous ranges of proportions are from 1 to 2000, preferably 100 to 1500, and most preferably 100 to 250, ppm.

The colloidal seeds are advantageously incorporated in the synthesis mixture in the form of a suspension, advantageously in an aqueous medium, preferably water, or another liquid component of the synthesis mixture. Less preferably they may be added in dry, but not calcined, form. It is believed that calcination significantly reduces the activity of small crystallites to act as seeds; similarly any other treatment that reduces the seeding activity of materials should be avoided. As used herein, the term "colloidal", when used of a suspension, refers to one containing discrete finely divided particles dispersed in a continuous liquid phase and preferably refers to a suspension that is stable, in the sense that no visible separation occurs or sediment forms, in a period sufficient for the use intended, advantageously for at least 10, more advantageously at least 20, preferably at least 100, and more preferably at least 500, hours at ambient temperature (23°C).

The maximum size of the particles for the suspension to remain stable (peptized) will depend to some extent on their shape, on the nature and pH of the continuous medium, as well as on the period during which the suspension must remain
5 usable. In general, the maximum dimension will be 1 μ m, advantageously 500, more advantageously 400, preferably 300, more preferably 200, and most preferably 100, nm. The particles may be of spherical, columnar, rod, coffin, platelet, or needle shapes. Where particles are platelets or
10 needles, the dimension referred to is their smallest dimension.

The minimum dimension is such that the particles do not dissolve or re-dissolve in the medium, and for crystallinity they must contain at least a small plurality, advantageously
15 at least two, preferably four, unit cells of the crystal. The minimum particle size is in general 5, advantageously 10, and preferably 20, nm. Mean particle sizes are generally in the range 5 to 1000, advantageously 10 to 300, more advantageously 10 to 200, and preferably 20 to 100, nm.
20 Advantageously at least 50%, more advantageously at least 80%, and more preferably at least 95%, by number, of the particles are greater than the given minima, smaller than the given maxima, or within the given ranges of particle size. Measurements of particle size may be effected by electron
25 microscopy, for example using a Philips SEM 515 unit.

If the product is desired in small particle size form, a larger number of smaller sized seeds is desirably employed. The smaller the particle size of the seeds, the lower the weight percentage that is effective. The crystals are
30 advantageously stirred into the synthesis mixture for a time sufficient to provide a uniform dispersion, this time being dependent primarily on the viscosity of the synthesis mixture, and also on the scale and type of the equipment, but ranging generally from 30 seconds to 10 minutes.

More especially, the invention provides processes and uses in which colloidal LEV structure type seeds are used in the manufacture of a phosphorus-containing crystalline molecular sieve.

5 A colloidal suspension of LEV may be obtained by synthesizing a LEV structure type molecular sieve by hydrothermal treatment of an appropriate synthesis mixture, and separating the product from the synthesis mixture, washing the product, and recovering the resulting wash
10 liquid.

Examples of the LEV structure type include Levyne, NU-3, ZK-20, ZSM-45 and SAPO-35.

The colloidal LEV seeds are especially suitable to provide crystalline molecular sieves of the CHA structure
15 type. Examples of such CHA materials are SAPO-, AlPO-, MeAPO-, MeAPSO-, ElAPSO- and ElAPO -47 and especially the corresponding -34 materials. In these formulae, El represents magnesium, zinc, iron, cobalt, nickel, manganese, chromium or mixtures of any two or more such elements. CHA
20 structure type seeds may also be used in synthesis of these materials. LEV and CHA structure type seeds may be used in the synthesis of SAPO-, AlPO-, MeAPO-, MeAPSO-, ElAPSO- and ElAPO- materials of the LEV structure type, e.g., the -35 materials. Where a material is referred to as, for example, a
25 SAPO material, this terminology includes the possibility that additional elements may be present, either in the framework or otherwise, as in the case discussed below, of Ni-SAPO.

Among these materials, SAPO-34 has been found to have considerable utility in catalysing the conversion of methanol
30 to light olefins, primarily those with 2 to 4 carbon atoms (see, for example, U.S. Patent No. 5 126 308, also incorporated by reference herein). It would be of value to be able to increase the proportion of ethylene in the product.

The present invention accordingly also provides a process for the manufacture of SAPO-34 in which the percentage area contribution of Broensted acid sites to the total OH area in the IR spectrum is at least 30%,
5 advantageously at least 50%, and preferably at least 60%, by a procedure in which the synthesis mixture contains colloidal crystalline molecular sieve crystals. In certain embodiments, percentage area contribution is at most 95%.

More especially, the invention further provides a
10 process for the manufacture of SAPO-34, which comprises treating a synthesis mixture having a molar composition appropriate for SAPO-34 formation and also containing colloidal OFF-type, CHA-type, or LEV-type seed crystals, advantageously of mean particle size of at most 400 nm, for a
15 time and at a temperature sufficient to form SAPO-34.

The process of the invention is capable of providing SAPO-34 in which the particle size is at most 0.75 μm , advantageously at most 0.5 μm . Advantageously the particle size distribution is such that 80 % (by number) of the
20 particles are within ± 10 % of the mean.

In a further aspect, the invention provides a process for the conversion of an oxygenate, especially methanol, to olefins which comprises contacting the oxygenate with a catalyst under conversion conditions, the catalyst comprising
25 SAPO-34 produced in accordance with the invention.

The olefins produced are advantageously light olefins, by which is to be understood an olefin mixture of which at least 50% by weight contain from 2 to 4 carbon atoms.

Referring now more especially to the Broensted acid site
30 aspect of the invention, it is believed (without the invention being limited by any theoretical considerations) that the Broensted acidity is important in the catalytic activity, especially in oxygenate to olefin conversion, of a molecular sieve, and that a molecular sieve in which the

bridged hydroxyl groups represent a high proportion of the hydroxyl groups in the crystal will have a high activity. Infra-red analysis of a highly active product of the invention (described as are the methods of measurement in more detail in the Examples below) shows that in the SAPO-34 OH region, 4000 to 3000 cm^{-1} , two peaks, at ~ 3620 and ~ 3595 cm^{-1} , are the main features, while less active samples show a number of bands in the range from 3750 to 3620 cm^{-1} , which are assigned to Al-OH, Si-OH, and P-OH groups on an external surface or on an internal defect.

A further IR spectrum characteristic associated with catalytic activity is a high peak intensity in the T-O asymmetric stretch region, at 1050 to 1150 cm^{-1} , intensity being indicated by both height and sharpness, i.e., a high level of internal crystallinity. It is accordingly believed that a correlation exists between high internal crystallinity, or crystal perfection, and a high contribution of Broensted OH groups to the total OH content of the material.

Further, in common with many other molecular sieves, the catalytic activity and stability of activity of SAPO-34 are in general terms greater the smaller the particle size.

The synthesis mixture for producing SAPO-34 according to the invention advantageously has a molar composition, apart from the colloidal seeds, within the following ranges:

P_2O_5	:	Al_2O_3		0.9 to 1.2	:	1
SiO_2	:	Al_2O_3		0.05 to 0.4	:	1
H_2O	:	Al_2O_3		10 to 100	:	1

30

together with an organic template, advantageously tetraethylammonium hydroxide (TEAOH), dipropylamine (DPA), isopropylamine or morpholine, or a mixture of two or more

such templates, in a proportion appropriate to yield SAPO-34. A preferred template mixture comprises TEAOH and DPA.

In a particularly advantageous embodiment of the invention the synthesis mixture advantageously contains a source of metallic elements, especially a Group VIII metal, more especially nickel. A convenient source of the metal is a water-soluble salt, for example the nitrate. The metal is advantageously present in a molar proportion calculated as oxide relative to Al_2O_3 within the range of 0.001 to 0.05, preferably 0.005 to 0.01. The presence of nickel enhances the catalytic activity at least in oxygenate conversion. Other suitable Group VIII metals include Fe and Co, while other suitable metals include Mn, Cr, Cu, Zn, Mg, Ti and Zr.

The sources of the materials may be any of those in commercial use or described in the literature, as may the preparation of the synthesis mixture.

The invention also provides the products of the processes and of the uses of the earlier aspects of the invention. The products, if required after cation exchange and/or calcining, have utility as catalyst precursors, catalysts, and separation and absorption media. They are especially useful in numerous hydrocarbon conversions, separations and absorptions. They may be used alone, or in admixture with other molecular sieves, in particulate form, supported or unsupported, or in the form of a supported layer, for example in the form of a membrane, for example as described in International Application WO 94/25151. Hydrocarbon conversions include, for example, cracking, reforming, hydrofining, aromatization, oligomerisation, isomerization, dewaxing, and hydrocracking (e.g., naphtha to light olefins, higher to lower molecular weight hydrocarbons, alkylation, transalkylation, disproportionation or isomerization of aromatics). Other conversions include the

reaction of alcohols with olefins and the conversion of oxygenates to hydrocarbons.

Conversion of oxygenates may be carried out with the oxygenate, e.g., methanol, in the liquid or, preferably, the vapour phase, in batch or, preferably, continuous mode. When carried out in continuous mode, a weight hourly space velocity (WHSV) based on oxygenate, of advantageously 1 to 1000, preferably 1 to 100, hour^{-1} may conveniently be used. An elevated temperature is generally required to obtain economic conversion rates, e.g., one between 300 and 600°C, preferably from 400 to 500°C, and more preferably about 450°C. The catalyst may be in a fixed bed, or a dynamic, e.g., fluidized or moving, bed.

The oxygenate feedstock may be mixed with a diluent, inert under the reaction conditions, e.g., argon, nitrogen, carbon dioxide, hydrogen, or steam. The concentration of methanol in the feedstream may vary widely, e.g., from 5 to 90 mole per cent of the feedstock. The pressure may vary within a wide range, e.g., from atmospheric to 500 kPa.

The following Examples, in which parts are by weight unless otherwise indicated, illustrate the invention. The source and purity of starting materials are those first given, unless indicated otherwise.

Example 1

This example illustrates the manufacture of a LEV-type zeolite of particle size suitable for use as seeds in the manufacture, inter alia, of phosphorus-containing crystalline molecular sieves.

In a first stage, 15.95 parts of sodium aluminate (Dynamit Nobel, 53 % Al_2O_3 , 41 % Na_2O , 6 % H_2O), 19.95 parts of sodium hydroxide (Baker, 98.6 %) and 5.58 parts of potassium hydroxide (Baker, 87.4 %) were dissolved in 151.06

parts of water, and heated to boiling until a clear solution was obtained. After cooling to room temperature, water loss was compensated, to form Solution A. 270.60 parts of colloidal silica (Ludox HS40, 40 % SiO₂) were mixed with 5 106.12 parts of choline chloride (R, Fluka) forming a viscous mass, and Solution A added with stirring at increasing speed as the viscosity decreased, together with 190 parts of rinse water, mixing then continuing for a further 5 minutes. The molar composition was:

10

1.95 Na₂O:0.24 K₂O:0.46 Al₂O₃:10 SiO₂:4.187 R:155 H₂O.

To 290 parts of this mixture, 0.49 parts of conventional LEV zeolite seeds were added, and a sample transferred to an 15 autoclave, where it was heated in a 120°C oven for 144 hours. The product was washed, recovered by centrifuging and dried overnight at 120°C. The product comprised spherical aggregates of from 2 to 2.5 µm, made up of ~100 nm particles, with an X-ray diffraction pattern (XRD) of ZSM-45, a zeolite 20 of LEV-type structure, as described in EP-A-107 370 (Mobil).

The product was used as seeds in the next stage, in which 8.38 parts of sodium aluminate, 10.53 parts of sodium hydroxide, 2.96 parts of potassium hydroxide, and 78.95 parts of water were treated as described above to form a Solution 25 A. Solution A was then added to a mixture of 142.42 parts of colloidal silica and 55.5 parts of choline chloride, together with 100.00 parts of rinse water and mixed as described above, with the addition of 0.68 parts of the first stage seeds. The reaction mixture was heated in an 30 autoclave at 120°C for 174 hours, the product recovered by washing, centrifuging and drying having an XRD similar to that of the first stage. The second supernatant of the washing procedure was not clear, and had a pH of 10.3. It was found to be a dispersion with a solids content of 2.3 %.

Analysis by scanning electron microscopy (SEM) and XRD showed ~100 nm unaggregated crystals with a ZSM-45 structure, LEV structure type.

5 Example 2

This example illustrates the manufacture of a chabasite dispersion suitable for use, in turn, for seeding in SAPO-34 manufacture. The seeds were prepared as follows:

10 A synthesis mixture was prepared as described in the first part of Example 1, except that as seeds the colloidal sol from the second supernatant of the second part of Example 1 was used, at a seeding level of 0.15% by weight of solids. The seeded synthesis mixture was heated in a stainless steel
15 autoclave for 96 hours at 120°C, with a heat-up time of 3 hours. The product, recovered by centrifuging and drying, had an XRD pattern corresponding to ZSM-45. The first supernatant was not clear and yielded, after centrifuging at 11000 rpm and further washing, a dispersion with solids
20 content 4.6%, of crystals of size about 100 nm, XRD showing the product to be ZSM-45, a LEV structure-type zeolite.

Solution A was prepared as described in Example 1 using the following components, in the proportions shown:

25	NaOH	61.66
	KOH	28.73
	Al(OH) ₃ (Alcoa, 99.3 %)	15.73
	H ₂ O	190.30

30 300.23 parts of colloidal silica and 168.89 parts of water were poured into a mixer, and Solution A added together with 12.65 parts of rinse water. After mixing for 5 minutes, 16 parts of the 4.6 % solids LEV slurry were added.

The molar composition of the synthesis mixture was:

3.8 Na₂O:1.12 K₂O:0.5 Al₂O₃:10 SiO₂:161 H₂O,
with 927 ppm seeds.

5

The synthesis mixture was heated in an autoclave to 100°C over 2 hours, and maintained at that temperature for 96 hours. After cooling, the content of the autoclave, a milky suspension, was washed five times with demineralized water and centrifuged at 9000 rpm. After taking a sample for XRD and SEM, the remainder was redispersed to form a colloidal solution, stable over several days, with a solids content of 6.4 %. The XRD of the product shows it to be chabasite, with a uniform particle size 100 x 400 nm.

15

Example 3

This example illustrates the manufacture of SAPO-34 of small particle size and uniform size distribution.

20 A synthesis mixture was prepared from the following components in the proportions shown.

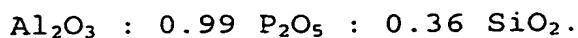
Solution		Component	Proportion
	A	Al ₂ O ₃ (Pural SB Condea 75%)	68.18
		H ₂ O	100.02
5	B	H ₃ PO ₄ (Acros, 85%)	115.52
		H ₂ O,	80.27
10	C	Colloidal Silica (Ludox AS40)	22.73
		H ₂ O, rinse	10.20
	D	TEAOH (Eastern Chemical, 40%)	182.85
	E	DPA (Fluka)	80.23
15	F	Seeds, 4.6 Wt.% LEV	31.95

Slurry A was prepared in a mixer, and Solution B added, when a viscous solution resulted. After leaving the solution to rest for 2 minutes, 26.84 parts of rinse water were added. After mixing the paste for 6 minutes, C was added, and mixed for 2 minutes before adding Solution D. Upon adding E with 70.72 parts of rinse water two phases were formed. After a further 3 minutes mixing a visually homogeneous solution resulted and after a further 10 minutes mixing the seeds F were added. The molar composition was:

Al₂O₃:P₂O₅:0.3 SiO₂:TEAOH:1.6 DPA:56 H₂O.
+ 1860 ppm by weight LEV seeds.

The seeded gel was heated for 60 hours at 175°C in a stainless steel autoclave. The solid product was recovered by centrifugation, washed 11 times with water to a conductivity of about 18 µs/cm, and dried at 120°C. XRD and SEM showed a pure SAPO-34 product with crystals between 0.2

and 1.3 μm , with a few crystals between 2 and 3 μm . Chemical analysis indicated a product of molar composition:

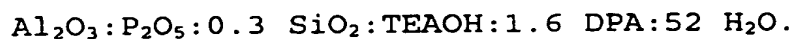


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In a similar manner a synthesis mixture was prepared from the following components in the proportions shown.

	Solution	Component	Proportion
10	A	Al ₂ O ₃ (Pural SB Condea 75 %)	68.06
		H ₂ O	100.15
15	B	H ₃ PO ₄ (Acros, 85 %)	115.74
		H ₂ O, including rinse	104.92
20	C	Colloidal Silica (Ludox AS40)	22.50
		H ₂ O, rinse	10.20
25	D	TEAOH (Eastern Chemical, 40 %)	183.31
		H ₂ O, rinse	43.17
30	E	DPA (Fluka)	80.79
		H ₂ O, rinse	26.27

Slurry A was prepared in a mixer, and Solution B added, 35 when a viscous mixture resulted. After mixing for 6 minutes, Solution C was added, and mixed for 2 minutes before adding Solution D which was mixed in for 5 minutes. When E was added, two phases were formed. After a further 15 minutes mixing a visually homogeneous mixture resulted. The 40 molar composition was:



The synthesis solution was divided, and to one sample a 6.4 % slurry of CHA zeolite, prepared as described in Example 2, was added to give a seeding level 410 ppm, the other sample remaining unseeded.

The unseeded sample was heated in a stainless steel autoclave at 175°C for 60 hours. The seeded sample was divided, one part being heated, without stirring, in a ptfe-lined autoclave for 60 hours at 175°C, and the other being heated with tumbling in a stainless steel autoclave for 60 hours at 175°C.

The samples were allowed to cool, and the product recovered by washing and drying at 120°C. In all cases, a pure SAPO-34 product was obtained, with a molar chemical constitution and crystal sizes as follows:

Unseeded: Al_2O_3 : 0.91 P_2O_5 : 0.33 SiO_2 , 1 to 10 μm

Seeded,

static: Al_2O_3 : 0.89 P_2O_5 : 0.31 SiO_2 , 0.2 to 1.5 μm

Seeded,

tumbled: Al_2O_3 : 0.91 P_2O_5 : 0.35 SiO_2 , ~0.5 μm .

The benefits of reduced crystal size and size distribution of seeding with colloidal chabasite seeds are apparent, especially when combined with tumbling.

Example 4

This example illustrates the use of colloidal Offretite seeds in the manufacture of SAPO-34. The colloidal Offretite was prepared as described in Example 2 of WO

97/03020. A synthesis mixture was prepared as described in Example 3, with the following molar composition:

Al_2O_3 : P_2O_5 : 0.3 SiO_2 : TEAOH : 1.6 DPA : 51 H_2O .

5

To this was added a portion of a 5.36 % solids content colloidal offretite slurry (crystal size below 100 nm) to give a seeding level of 203 ppm. Hydrothermal treatment and product recovery were carried out as described in Example 3.

10 The product obtained was pure SAPO-34, the particle size of crystals being mainly between 0.2 and 1.3 μm , with a few crystals between 2 and 3 μm present.

Comparative Example A

15

This example illustrates the use of powdered LEV, contaminated with some Offretite, in SAPO-34 manufacture. To the same synthesis mixture prepared for use in Example 4 were added a LEV powder in a proportion to give a seed level

20 of 217 ppm. The powder was mixed into the synthesis mixture gel by shaking the gel in a polypropylene bottle for 2 minutes. Hydrothermal treatment and product recovery were carried out as described in Example 4. The product was pure SAPO-34, with the majority of the crystals of size between

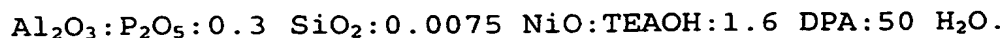
25 0.5 and 2.5 μm . Comparison of this example with Example 4 shows that colloidal seeds at approximately the same weight ratio yield smaller crystals.

Example 5

30

In this example, the effect of seeding on Ni-SAPO 34 manufacture was examined. The synthesis mixture was prepared as in Example 3, except that sufficient nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Fluka) was added to Solution A to

give a synthesis mixture of molar composition:



5 The mixture was divided into two parts, one being seeded with CHA slurry, 6.4 % solids content, to a seeding level of 409 ppm. The seeded and unseeded samples were each heated in a stainless steel autoclave for 60 hours at 175°C. After cooling, the products were recovered, washed, and dried at 10 120°C. In both cases, a pure SAPO-34 phase was recovered, with molar chemical constitutions and crystal sizes as follows:

Unseeded: Al_2O_3 : 0.88 P_2O_5 : 0.36 SiO_2 : 0.0040 NiO,
15 1 to 10 μm

Seeded: Al_2O_3 : 0.84 P_2O_5 : 0.31 SiO_2 : 0.0042 NiO,
0.2 to 1.5 μm .

20 Again, the benefit of seeding in producing smaller
 crystals is apparent.

The two samples made as described above were examined by diffuse reflectance FTIR to establish their crystal quality and Brønsted acidity. The IR spectra were obtained in a conventional high temperature DRIFT cell using KBr diluted samples (about 4 % sample in dry KBr), the samples being dehydrated before testing at 200 to 300°C under vacuum. The spectra, obtained using 64 scans at 4 cm⁻¹ resolution, were analysed using Gaussian-Lorentzian peaks to determine locations and relative areas and shapes.

The spectra of the seeded and unseeded products of the example were inspected in the region between wave numbers 1400 and 1000cm⁻¹ and the main peaks attributable to framework T-O stretching were measured. In the Table below are set out

the centre locations, peak heights and peak widths (C, H, W) of the three main bands in the region.

		C, H, W	C, H, W	C, H, W
5	Seeded	1106/8.7/51	1135/12.3/54.7	1179/6.7/65.5
	Unseeded	1082/1.4/90	1129/2.1/71	1190/0.9/90.6

The seeded sample has, as is apparent from the Table, by far the highest and sharpest peaks, and hence the highest
10 internal crystallinity.

The sole figure of the accompanying drawings shows the region between wave numbers 3800 and 3450 cm^{-1} .

Referring now to the figure, the locations, heights and widths of the main peaks attributable to the bridged hydroxyl
15 groups are shown for the samples. The band at ≈ 3620 is attributed to undisturbed Broensted OH groups in 8-membered rings while that at ≈ 3595 is attributed to such OH groups interacting with framework oxygen or OH groups located in the 6-membered rings. Measurement of the contribution (by area)
20 of these bands to the total area in the OH region gives the results in the Table below:

	Sample	% Area Contribution
	Seeded	62
25	Unseeded	21

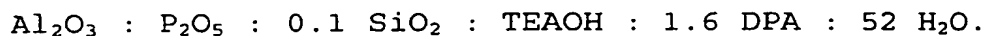
Clearly, the seeded sample has the higher percentage area contribution from the Broensted acid sites, despite the fact that this sample has a lower particle size, and hence a
30 larger surface/volume ratio. From this it is tentatively concluded that the remaining peaks in the 3800 to 3620 cm^{-1} range are associated with internal defects rather than surface hydroxyl groups, and postulated that products with high percentage area contribution of Broensted acid OH groups

to the total OH area are materials with a high level of internal crystal perfection.

Example 6

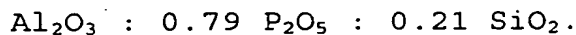
5

This example illustrates the use of CHA seeds in the manufacture of SAPO-34 with a silicon content different from that of Example 3. The synthesis solution was prepared as described in Example 3, but with components in proportions to
10 give the following molar composition:



A slurry of 6.4 % solids content of CHA seeds was added
15 to give a seed content of 397 ppm.

The mixture was hydrothermally treated as described in Example 3, and the product recovered in the same way. It was pure SAPO-34, with most crystals in the range 0.2 to 1.5 μm , with a few crystals of size in the 2 to 4 μm range also
20 present. The product analysed as



Example 7

25

Example 6 was repeated, except that the silica content was varied to give a molar composition of the synthesis

mixture of:

Al_2O_3 : P_2O_5 : 0.45 SiO_2 : TEAOH : 1.6 DPA : 52 H_2O
with 397 ppm CHA seeds.

5

The hydrothermal treatment was as described in Example 3; the product was pure SAPO-34 of particle size between 0.2 and 1.5 μm . Chemical analysis:

10

Al_2O_3 : 0.92 P_2O_5 : 0.42 SiO_2 .

15

The yields from Examples 6 and 7, and the static seeded part of the second part of Example 3, the synthesis mixtures of which differed primarily in their silicon contents, were as follows:

Example 6, 0.1 SiO_2 ; yield 7.8 %
3, 0.3 SiO_2 ; yield 12.5 %
7, 0.45 SiO_2 ; yield 12.7 %.

20

Comparative Example B

In Examples 5 to 7, hydrothermal treatment was carried out in a static autoclave. In this and following examples, the influences of stirring and tumbling on the properties of SAPO-34 were examined, this example employing an unseeded synthesis mixture of a molar composition similar to that of the second part of Example 3, but with 51 moles of H_2O rather than 52. Hydrothermal treatment was carried out by heating the synthesis mixture in a stainless steel autoclave from room temperature to 175°C over 6 hours, with stirring at 120 rpm, and maintained at 175°C for 60 hours with continued stirring. Recovery was as described in Example 3. The

product was a mixture of SAPO-34, SAPO-18, with some SAPO-5, the crystals being within the range of 0.2 to 1 μm .

Example 8

5

This example illustrates the effect of stirring an Offretite seeded synthesis mixture during hydrothermal treatment. Colloidal (<100 nm) Offretite seeds were added from a 5.36 % solids content Offretite slurry, the resulting
10 molar composition of the seeded mixture being:

Al_2O_3 : P_2O_5 : 0.3 SiO_2 : TEAOH : 1.6 DPA : 54 H_2O
plus 0.19 weight % seeds.

15 The synthesis mixture was divided into two parts. One part (A) was placed in a stainless steel autoclave equipped with a 120 rpm stirrer and heated from room temperature to 175°C over 6 hours with stirring, and maintained at 175°C for 60 hours with continued stirring. A second part (B) was
20 heated without stirring from room temperature to 175°C over 2 hours, and maintained at 175°C for 48 hours, with a sample (C) being taken at 24 hours. After recovery and drying, the products were analysed by SEM and XRD.

Sample A : SAPO-34, contaminated with SAPO-18 and some
25 SAPO-5, crystals between 0.2 and 1.0 μm .

Sample B : Pure SAPO-34, with crystal size 0.5 to 2 μm .

Sample C : SAPO-34 with some amorphous material, crystals between 0.2 and 1.5 μm .

30 Example 9

This example illustrates the effect on Ni-SAPO-34 manufacture of agitation during the warm-up period of hydrothermal treatment, followed by static heat-soaking. A

nickel-containing synthesis mixture was prepared, following the procedure described in Example 4, to produce a mixture of molar composition:

5 $\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:0.3 \text{ SiO}_2:0.0076 \text{ NiO:TEAOH:1.6 DPA:52 H}_2\text{O}$.

The mixture was divided into two parts, of which one, sample A, was seeded with the CHA seeding slurry used in Example 5 to give a seed content of 202 ppm, the other,
10 sample B, remaining unseeded. Both samples were transferred to stainless steel autoclaves, which were placed in an oven and mounted on a horizontal shaft rotatable at 60 rpm. The autoclaves were tumbled for a 2 hour period of heating to 175°C; tumbling then ceased and the temperature kept at 175°C
15 for 60 hours.

After cooling, the products were recovered by centrifugation, washed, and dried at 120°C. XRD showed that both products were pure Ni-SAPO-34. Sample A comprised crystals of particle size about 1 μm , with damaged surfaces.
20 Sample B comprised crystals of size ranging up to 10 μm , many crystals being fragmented.

The example shows that seeding is required to bring the particle size down to the desired levels even with initial tumbling.

25

Example 10

This example illustrates the use of a SAPO-34 seed slurry in SAPO-34 manufacture.

30 To a synthesis mixture of the molar composition set out in the second part of Example 3 was added a 10% slurry of SAPO-34, prepared as described in the second part of Example 3 with tumbling, to give a seeding level of 0.1% (1000 ppm). The seeded mixture was heated in a stainless steel autoclave

at 175°C for 48 hours. The mixture was allowed to cool, and the product recovered and identified as pure SAPO-34 with crystal sizes ranging from 0.5 to 4 μm . The example illustrates that while colloidal SAPO-34 crystals are effective in SAPO-34 manufacture they are not as effective as CHA or LEV structure type zeolite seeds.

Example 11

In this example the effectiveness in catalysing the methanol to olefin conversion of the products made and discussed in Example 5 was measured. In a bench scale fixed bed reactor maintained at 450°C methanol diluted with nitrogen (total pressure-atmospheric, partial pressure of methanol 0.12) was passed over a catalyst at WHSV (based on methanol) of 1 hr^{-1} and a GHSV (based on methanol plus nitrogen) of about 5500 hr^{-1} . After 1 hour on stream at 100 % methanol conversion, the results were as shown in the Table.

	Example 5	Example 5
Yield, %	Seeded	Unseeded
C ₂ =	50.1	47.9
C ₃ =	28.0	33.4
25 C ₂ = + C ₃ = + C ₄ =	85.6	91.4
C ₁ to C ₄ sats.	11.0	6.1

The yield of the more desirable ethylene is increased by about 5% using the product obtained with seeding compared with the unseeded product.

CLAIMS

1. A process for the manufacture of a crystalline molecular sieve containing phosphorus in its framework, which process
5 comprises treating a synthesis mixture comprising elements necessary to form the phosphorus-containing molecular sieve and colloidal crystalline molecular sieve seeds for a time and at a temperature appropriate to form the desired molecular sieve.
- 10 2. A process as claimed in claim 1, wherein the phosphorus-containing molecular sieve is an aluminophosphate or a silica-aluminophosphate, optionally containing other elements.
- 15 3. A process as claimed in claim 1 or claim 2, wherein the phosphorus-containing molecular sieve is of the CHA or LEV structure type.
- 20 4. A process as claimed in claim 1 or claim 2, wherein the phosphorus-containing molecular sieve is SAPO-34.
5. A process as claimed in claim 4, wherein the percentage area contribution of Brønsted acid sites to the total OH
25 area in the IR spectrum is at least 30%.
6. A process as claimed in claim 5, wherein the said contribution is at least 50%.
- 30 7. A process as claimed in any one of claims 4 to 6, wherein the SAPO-34 is Ni-SAPO-34.
8. A process as claimed in any one of claims 1 to 7, wherein the seeds are of structure type LEV, OFF, or CHA.

9. A process as claimed in any one of claims 1 to 7, wherein the seeds are of Levyne, ZSM-45, Chabasite, Offretite, or SAPO-34.

5

10. A process as claimed in any one of claims 1 to 9, wherein the seeds are present in a proportion within the range of 1 to 2000 ppm, based on the total weight of the synthesis mixture.

10

11. A process as claimed in claim 10, wherein the proportion is within the range of from 100 to 1500 ppm.

12. A process as claimed in claim 10, wherein the proportion
15 is within the range of from 100 to 250 ppm.

13. A process as claimed in any one of claims 1 to 12, wherein the seeds are incorporated in the synthesis mixture in the form of a suspension.

20

14. A process as claimed in any one of claims 1 to 13, wherein the particle size of the seeds is within the range of from 5 to 1000 nm.

25 15. A process as claimed in claim 14, wherein the particle size is within the range of from 10 to 300 nm.

16. A process as claimed in claim 14, wherein the particle size is within the range of from 20 to 100 nm.

30

17. A process as claimed in any one of claims 1 to 16, wherein the phosphorus-containing molecular sieve is of a first structure type and the seeds are of a second structure type.

18. A process as claimed in claim 17, wherein the first structure type is CHA and the second structure type is LEV.

5 19. A molecular sieve whenever produced by a process as claimed in any one of claims 1 to 18.

20. SAPO-34 in which the percentage area contribution of Broensted acid sites to the total OH area in the IR spectrum
10 is at least 30%, obtainable by a process as claimed in any one of claims 1 to 18.

21. A molecular sieve as claimed in claim 19 or claim 20, in particulate or layer form.

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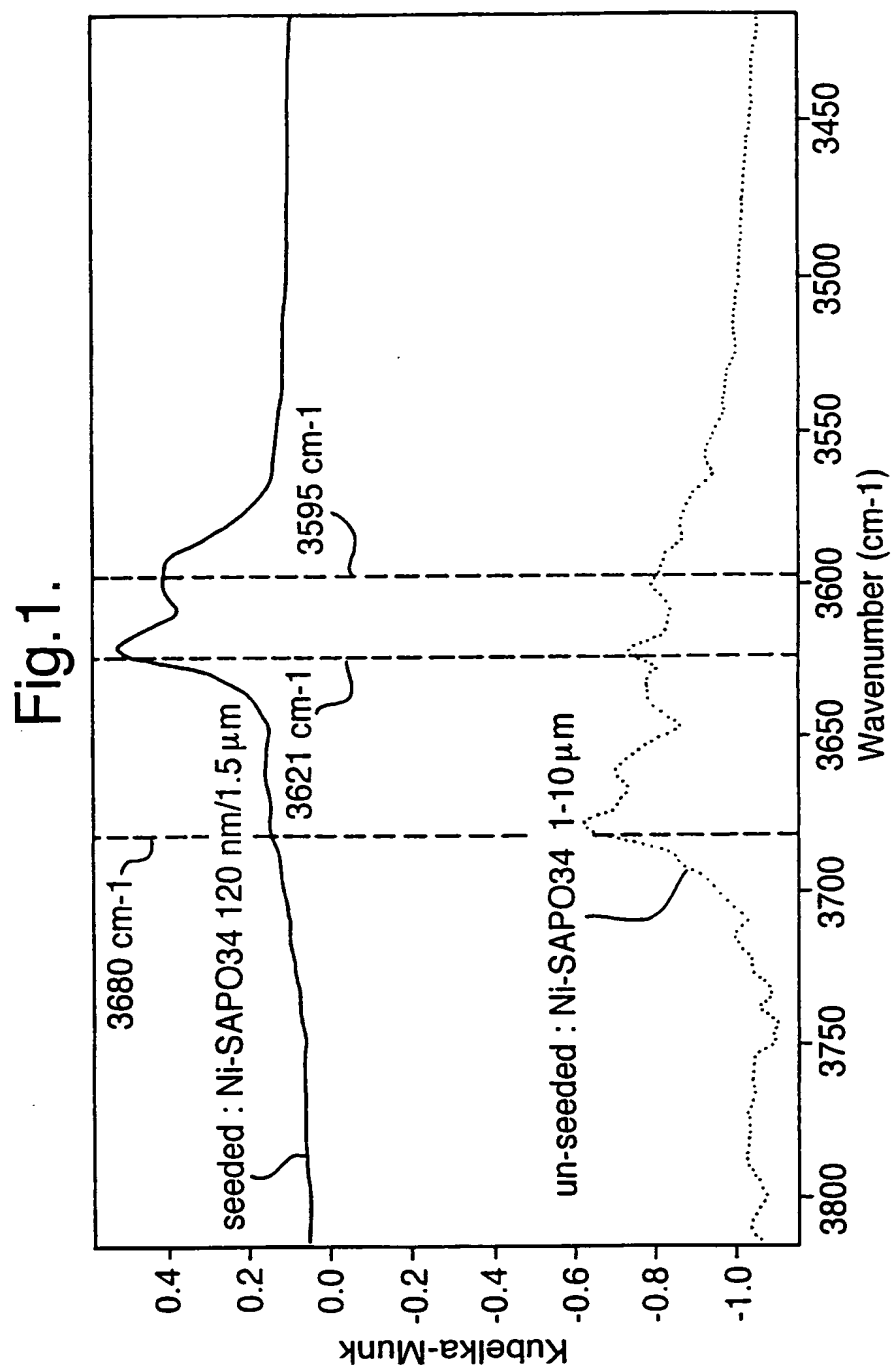
22. A process for the conversion of an oxygenate to olefins which comprises contacting the oxygenate under catalytic conversion conditions with a molecular sieve as defined in any one of claims 19 to 21.

20

23. The use of the molecular sieve as claimed in any one of claims 19 to 21, if desired after washing, cation exchange, or calcining, in hydrocarbon conversion, adsorption, or separation.

25

24. The use, in the synthesis of a phosphorus-containing crystalline molecular sieve of colloidal crystalline molecular sieve seed crystals to control the particle size of the product, or to accelerate the formation of the product,
30 or both to control the particle size and accelerate the formation of the product.



INTERNATIONAL SEARCH REPORT

International Application No

PC/GB 99/02480

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B37/04 C01B37/06 C01B37/08 B01J29/04 C10G3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 753 485 A (EXXON CHEMICAL PATENTS INC) 15 January 1997 (1997-01-15) claims 1,5-7,13-15 page 2, line 7 - line 33 page 3, line 12 - line 48	1,13-16, 19,21, 23,24
A	---	8-12,17
X	EP 0 753 484 A (EXXON CHEMICAL PATENTS INC) 15 January 1997 (1997-01-15) claims 1-11 page 2, line 14 - line 32 page 3, line 10 - line 43	1,13-16, 19,21, 23,24
A	---	8-12,17
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

16 November 1999

Date of mailing of the international search report

23/11/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PL./GB 99/02480

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 110 650 A (MOBIL OIL CORP) 13 June 1984 (1984-06-13)</p> <p>claims 1,9-11,13,14 page 3, line 5 - line 16 examples 1,5</p> <p>---</p>	<p>1,13-16, 19,21, 23,24</p>
A	<p>WO 95 21792 A (CHEVRON USA INC) 17 August 1995 (1995-08-17) page 19, line 3 -page 23, line 11</p> <p>---</p>	<p>1,2,24</p>
A	<p>US 5 370 851 A (WILSON STEPHEN T) 6 December 1994 (1994-12-06) page 1, line 6 - line 14 column 5, line 12 - line 16 examples 1-3</p> <p>-----</p>	<p>1,2,24</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02480

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0753485	A	15-01-1997	NONE	
EP 0753484	A	15-01-1997	NONE	
EP 0110650	A	13-06-1984	AU 564738 B	27-08-1987
			AU 2151183 A	31-05-1984
			BR 8306419 A	26-06-1984
			CA 1213576 A	04-11-1986
			DK 531283 A, B,	23-05-1984
			JP 1776025 C	28-07-1993
			JP 4063010 B	08-10-1992
			JP 59131521 A	28-07-1984
			NZ 206295 A	10-09-1986
			ZA 8308722 A	31-07-1985
WO 9521792	A	17-08-1995	US 5501848 A	26-03-1996
			AU 1699195 A	29-08-1996
US 5370851	A	06-12-1994	US 5437781 A	01-08-1995